Simulation of hydrogen storage tank packed with metal-organic framework

Jinsheng Xiaoa,b,*, Min Huc, Pierre Bénardb, Richard Chahineb

a Hubei Key Laboratory of Advanced Technology for Automotive Components, School of Automotive Engineering, Wuhan University of Technology, Hubei 430070, China
b Hydrogen Research Institute, Université du Québec à Trois-Rivières, QC G9A 5H7, Canada
c School of Materials Science and Engineering, Wuhan University of Technology, Hubei 430070, China

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Abstract
Hydrogen adsorption in high surface metal-organic framework (MOF) has generated significant interest over the past decade. We studied hydrogen storage processes of MOF-5 hydrogen storage systems with adsorbents of both the MOF-5 powder (0.13 g/cm³) and its compacted tablet (0.30 g/cm³). The charge–discharge cycles of the two MOF-5 adsorbents were simulated and compared with activated carbon. The physical model is based on mass, momentum and energy conservation equations of the adsorbent-adsorbate system composed of gaseous and adsorbed hydrogen, adsorbent bed and tank wall. The adsorption process was modeled using a modified Dubinin–Astakhov (D–A) adsorption isotherm and its associated variational heat of adsorption. The model was implemented by means of finite element analysis software Comsol Multiphysics™, and the system simulation platform Matlab/Simulink™. The thermal average temperature from Comsol simulation is used to fill the gap between the system model and the multi-dimensional models. The heat and mass transfer feature of the model was validated by the experiments of activated carbon, the simulated pressure and temperatures are in good agreement with the experimental results. The model was further validated by the metal-organic framework of Cu-BTC and is being extended its application to MOF-5 in this study. The maximum pressure in the powder MOF-5 tank is much higher than that in the activated carbon tank due to the lower adsorbent density of MOF-5 and resulting lower hydrogen adsorption. The maximum pressure in the compacted MOF-5 tank is a little bit lower than that in the activated carbon tank due to the higher adsorbent density and resulting higher hydrogen adsorption. The temperature swings during the charge–discharge cycle of both MOF-5 tanks are higher than that of the activated carbon tank. These are caused mainly by pressure work in the powder MOF-5 tank and by adsorption heat in the compacted MOF-5 tank. For both MOF-5 hydrogen storage systems, the lumped parameter models implemented by Simulink agree well with experimental pressures and with pressures and thermal average temperatures from Comsol simulation.

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1. Introduction

Hydrogen storage is a bottleneck for the widespread usage of hydrogen as an energy carrier. Hydrogen adsorption in high surface metal-organic framework (MOF) has generated a significant amount of interest over the past decade due to its high gravimetric storage density, fast kinetics and complete reversibility. The metal-organic framework MOF-5 has attracted significant attention due to its ability to store large quantities of hydrogen, by mass, up to 10 wt.% absolute at 70 bar and 77 K, and the increased volumetric hydrogen uptake of MOF-5 will be achieved by powder densification [1,2].

A number of researches about adsorptive hydrogen storage on metal-organic frameworks (MOFs) have been carried out in recent years. Peng et al. [3] used the computational fluid dynamics (CFD) method to simulate the charge and discharge cycle of MOF-5 hydrogen storage system. The low thermal conductivity of the metal-organic framework MOF-5 could limit performances in applications requiring rapid gas uptake and release, so Liu et al. [4] systematically studied the impacts of varying expanded natural graphite (ENG) content and compact density on the thermal conductivity, surface area, specific heat capacity, and crystallinity of densified MOF-5/ENG composites. Juan et al. [5] compared the hydrogen storage properties for a variety of adsorbents including two activated carbons and a metal-organic framework (MOF-5) on gravimetric and volumetric bases. Schlichtenmayer et al. [6] compared the hydrogen adsorption properties of three adsorbents simulated and compared with activated carbon.

In this work we studied hydrogen storage processes of MOF-5 hydrogen storage systems with adsorbents of both the MOF-5 powder (0.13 g/cm³) and its compacted tablet (0.30 g/cm³). The charge–discharge cycles of these two MOF-5 adsorbents are simulated and compared with activated carbon. The physical model is based on mass, momentum and energy conservation equations of the adsorbent-adsorbate system composed of gaseous and adsorbed hydrogen, adsorbent bed and tank wall. The adsorption process was modeled using a modified Dubinin–Astakhov (D–A) adsorption isotherm and its associated variable heat of adsorption. The model was implemented by means of finite element analysis software Comsol Multiphysics™, and the system simulation platform Matlab/Simulink™.

2. Models of transport and adsorption phenomena

2.1. Distributed parameter model

Mass conservation equation can be written as:

\[
\frac{\partial (\rho_p \rho_i)}{\partial t} + \nabla \left( \rho_i \boldsymbol{v} \right) = S_m
\]

The mass source term \(S_m\) due to adsorption or desorption can be expressed as:

\[
\Delta H \text{ isosteric heat of adsorption, } J/mol
\]

\[
c_{pg} \text{ specific heat capacity of hydrogen gas, } J/(kg K)
\]

\[
c_{ps} \text{ specific heat capacity of adsorbent, } J/(kg K)
\]

\[
h_w \text{ heat transfer coefficient, } W/(m^2 K)
\]

\[
h_i \text{ specific enthalpy of inflow hydrogen flow, } J/kg
\]

\[
h_o \text{ specific enthalpy of outflow hydrogen flow, } J/kg
\]

\[
k_{eff} \text{ effective thermal conductivity of activated carbon bed, } W/(m K)
\]

\[
k_g \text{ thermal conductivity of hydrogen gas, } W/(m K)
\]

\[
k_a \text{ thermal conductivity of adsorbent, } W/(m K)
\]

\[
M_{H2} \text{ molecular mass of hydrogen, } kg/mol
\]

\[
m_a \text{ mass of adsorbed phase hydrogen, } kg
\]

\[
m_g \text{ mass of gas phase hydrogen, } kg
\]

\[
m_t \text{ total mass of hydrogen in tank, } kg
\]

\[
n_a \text{ absolute adsorption amount per unit adsorbent, mol/kg}
\]

\[
n_0 \text{ limit adsorption amount per unit adsorbent, mol/kg}
\]

\[
p \text{ pressure, Pa}
\]

\[
Q \text{ adsorption heat, } W/m^3
\]

\[
U \text{ total internal energy, W}
\]

\[
W \text{ pressure work, } W/m^3
\]

\[
R \text{ universal gas constant, } 8.314 J/(mol K)
\]

\[
T \text{ temperature, K}
\]

\[
\vec{u} \text{ Darcy velocity vector, } m/s
\]

Greek symbols

\[
\alpha_{D-A} \text{ enthalpic factor, J/mol}
\]

\[
\beta_{D-A} \text{ entropic factor, J/(mol K)}
\]

\[
\beta_T \text{ volume expansion coefficient, } 1/K
\]

\[
\varepsilon_b \text{ bed porosity}
\]

\[
\phi \text{ viscous dissipation, } W/m^3
\]

\[
\kappa \text{ permeability, } m^2
\]

\[
\mu \text{ dynamic viscosity of hydrogen, } Pa s
\]

\[
\rho_g \text{ density of hydrogen gas, } kg/m^3
\]

\[
\rho_p \text{ particle density of adsorbent, } kg/m^3
\]
\[ S_m = \frac{\partial}{\partial t} (\rho_b q_b) = -(1 - \epsilon_b) \rho_b M_t \frac{\partial n_a}{\partial t} \] (2)

The bed density \( \rho_b \) is further expressed with bed porosity and particle density as \( \rho_b = (1 - \epsilon_b) \rho_p \), and the mass ratio of adsorbate to adsorbent \( q_b \) [kg/kg] is expressed with the absolute adsorption amount \( n_a \) [mol/kg] and the molecular mass of hydrogen gas as \( q_b = M_t \epsilon_b n_a \).

Momentum conservation equation used in Comsol is simplified as Darcy’s Law:
\[ \vec{v} = -\frac{k}{\mu} \nabla p \] (3)
where \( k = D_p \epsilon_b^2/[150(1 - \epsilon_b)^2] \) is the permeability, \( \mu \) is the dynamic viscosity of hydrogen gas, \( D_p \) is the mean diameter of adsorbent particles.

Energy conservation equation can be written as:
\[ (\rho c_p)_{\text{eff}} \frac{\partial T}{\partial t} + \rho_g c_{pg} \vec{v} \cdot \nabla T = \nabla \cdot (k_{\text{eff}} \nabla T) + Q + W + \Phi \] (4)

The effective thermal conductivity simply adopts the rule of mixture:
\[ k_{\text{eff}} = \epsilon_a k_g + (1 - \epsilon_b) k_s \] (5)
where \( k_a \) and \( k_s \) are the thermal conductivities of hydrogen gas and adsorbent, respectively. The contribution of adsorbed phase of hydrogen to the effective heat capacity is considered in following expression:
\[ (\rho c_p)_{\text{eff}} = \epsilon_a \rho_g c_{pg} + (1 - \epsilon_b) \rho_p (c_{pa} + \epsilon_a c_{pu}) \]
\[ = \epsilon_a \rho_g c_{pg} + \rho_p n_a M_t c_{pa} + \rho_c c_{pu} \] (6)
where the specific heat capacity of gas phase is used for the approximation of the adsorbed phase, because the adsorbed gas above the critical temperature behaves as compressed gas in the feature of specific heat capacity, i.e., \( c_{pa} = c_{pg} \).

The source terms of adsorption heat, pressure work and viscous dissipation can be written as:
\[ Q = S_m \Delta H \frac{\partial n_a}{\partial t} \] (7)
\[ W = \epsilon_b \beta_T D_p \frac{\partial p}{\partial t} = \epsilon_b \beta_T \left( \frac{\partial \vec{p}}{\partial t} + \vec{v} \cdot \nabla p \right) = \beta_T \left[ \epsilon_b \frac{\partial \vec{p}}{\partial t} + \vec{v} \cdot \nabla p \right] \] (8)
\[ \Phi = \frac{\mu}{2} : \nabla \vec{v} = \mu \left[ \nabla \vec{v} + (\nabla \vec{v})^T - \frac{2}{3} (\nabla \cdot \vec{v}) I \frac{1}{2} \right] : \nabla \vec{v} \] (9)
where \( \Delta H \) is the isosteric heat of adsorption, \( \vec{u} \) is physical velocity in the porous channels, \( \vec{u} = \epsilon_b \vec{u} \) is the superficial velocity or Darcy’s velocity through porous media. \( \beta_T \) is the volumetric thermal expansion coefficient, \( \beta_T = 1/T \) for ideal gas. And \( I \) is the shear stress tensor, and \( I \) is the unit tensor. The simulations show that the effect of viscous dissipation on the temperature distribution in the hydrogen storage tank is very small and can be neglected.

### 2.2. Lumped parameter model

The rate of change of hydrogen mass in the storage tank is in equilibrium with the net hydrogen flow rate through the boundary of the tank. The mass balance equation can thus be expressed as:
\[ \frac{dm_t}{dt} = \dot{m}_i - \dot{m}_a \] (10)
where \( \dot{m}_i \) is the mass total mass of hydrogen in the tank, \( \dot{m}_i \) and \( \dot{m}_a \) is the mass flow rates flowing into and out of the tank, respectively.

With the changes of both kinetic and potential energies ignored, the energy balance for the storage tank, including its wall, can be expressed as:
\[ \frac{dU}{dt} = \dot{m}_i h_i - \dot{m}_a h_a - Q + \frac{dm_t}{dt} \Delta H \] (11)
where \( U = (m_c c_v + m_a c_w + m_e c_p)T \) and \( Q = h_a A_s (T - T_1) \).

Then the pressure is calculated from the ideal gas equation of state:
\[ p = \frac{m_g ZRT}{M_t V_b} = \frac{(m_t - m_a) ZRT}{M_t V_b} \] (12)
where \( m_g = m_t - m_a = m_t - n_e M_t n_a \), and \( m_a \) and \( m_e \) are the masses of hydrogen in adsorbed and gas phases, respectively, \( Z \) is the compressibility factor of hydrogen gas, \( R \) is the universal gas constant.

In order to compare with the lumped parameter temperature, a thermal average temperature is calculated from the temperature distribution obtain from distributed parameter model by the integrations over the tank volume:
\[ T_c = \frac{\int \rho c_p \text{eff} T dV}{\int \rho c_p \text{eff} dV} \] (13)

![Fig. 1 – Geometric model and finite element mesh.](image-url)
In cylinder coordinate system for axisymmetrical geometry, the differential volume can be expressed as \( dV = 2\pi r dr dz \).

### 2.3. Adsorption model

A modified Dubinin–Astakhov (D–A) adsorption model \([10]\) is used to describe the adsorption isotherm for MOF-5 and activated carbon (AC). The absolute adsorption is given by the following equation:

\[
\frac{\partial n_a}{\partial \tau} = n_{max} \left( \frac{RT}{\alpha_{D-A} + \beta_{D-A} T} \ln \left( \frac{p_0}{p} \right) \right)^m \left[ \frac{1}{\ln(p_0/p)} \right] \frac{1}{\alpha_{D-A}} \alpha_{D-A} \frac{\partial T}{\partial \tau} + \frac{1}{\beta_{D-A} T} \frac{\partial \beta_{D-A}}{\partial \tau}
\]

(15)

where \( R \) is the universal gas constant, \( T \) and \( p \) are the temperature and pressure, respectively. The exponent \( m \) is allowed to vary and is normally between 1 and 2 for adsorption of various gases on most adsorbents, and for hydrogen adsorption on MOF-5 and activated carbon, \( m \) equals to 2. The fitted parameters, such as, limit adsorption amount \( n_{max} \), limit pressure \( p_0 \), enthalpic factor \( \alpha_{D-A} \), and entropic factor \( \beta_{D-A} \), are taken from references \([10,14,15]\). Based on the chain-rule for differentiating composite functions, the partial derivative of the absolute adsorption in the source term of the mass conservation Eq. (1) can be written as:

\[
\frac{\partial n_a}{\partial \tau} = n_{max} \left( \frac{RT}{\alpha_{D-A} + \beta_{D-A} T} \ln \left( \frac{p_0}{p} \right) \right)^m \left[ \frac{1}{\ln(p_0/p)} \right] \frac{1}{\alpha_{D-A}} \alpha_{D-A} \frac{\partial T}{\partial \tau} + \frac{1}{\beta_{D-A} T} \frac{\partial \beta_{D-A}}{\partial \tau}
\]

Here the equilibrium absolute adsorption amount is used for simplicity considering the slow charging rate of current case. Based on the Dubinin–Astakhov model of adsorption, when \( m = 2 \), the isosteric heat of adsorption is obtained as:

\[
\Delta H = \alpha_{D-A} \sqrt{\ln(n_{max}/n_a)}
\]

(16)

### 3. Model parameters and validation

#### 3.1. Geometric model

The hydrogen storage tank is a stainless steel container packed with adsorbents and is put into a Dewar flask filled with coolant (room temperature water or liquid nitrogen). Fig. 1 shows an axisymmetric geometry model in Comsol. The volume of the tank is 2.5 L. The inner and outer radii at the entrance of the hydrogen storage tank are 0.004 m and 0.005 m respectively. The internal and external radii in the middle of the tank are 0.0469 m and 0.0508 m, respectively. The internal and external heights of the tank are 0.45 m and 0.454 m, respectively. To monitor the variations of pressure, temperature and adsorption density in the tank, we chose eight monitoring points, labeled as C1 (0, −0.09875), C2 (0, −0.14375), C3 (0, −0.18875), C4 (0, −0.23375), C5 (0, −0.27875), C6 (0, −0.32375), C7 (0.02345, −0.24875) and Cw (0.0469, −0.23375). The first six points are located along the symmetry axis of the hydrogen storage tank while the other two points Cr and Cw are, respectively, located at halfway and vicinity to the tank wall.

The mesh of the model is generated by Free Mesh of Comsol in which we can control mesh density as Extra fine mesh. It consists of 1516 triangular elements and 864 nodes, and the number of degrees of freedom to be solved is 5898. The similar mesh sensitive analysis as in reference \([16]\) is carried out for Finer mesh, Extra fine mesh and Extremely fine mesh in Comsol. The Extremely fine mesh does not increase the accuracy too much but double the run time. The Finer mesh has stability problem of numerical computation. Therefore, we adopt the Extra fine mesh in this study.

The time step for numerical simulations is set as 1 s in the current simulations. Time step taken by Comsol solver is set as Free so that the solver may subdivide the preset time step to obtain convergent solution for each time step. The preset time step is determined by looking at the actual average time step during the trial running of the model. The computation takes about 3 min for a typical case in a popular personal computer.

### 3.2. Material properties

The hydrogen storage system mainly contains adsorbents (powder MOF-5, MOF-5 compacted tablet and activated carbon), hydrogen, room temperature water or liquid nitrogen, stainless steel container and Dewar flask. We assume hydrogen is an ideal gas. The values of the fitted parameters of D–A model are shown in Table 1. The parameter values of the modified D–A model given in Table 1 are obtained by fitting experimental data ranging from 77 K to 300 K for powder MOF-5 \([14]\) and from 77 K to 295 K for compacted MOF-5 \([15]\). The material properties are given in Tables 2 and 3.

There are three porosities: particle, bed and total porosities. The particle porosity \( \epsilon_p \) is the intraparticle voidage of an adsorbent particle. The bed porosity \( \epsilon_b \) is the interparticle voidage of a packed bed. The relation among these three porosities is \( \epsilon_t = \epsilon_b + (1-\epsilon_b) \epsilon_p \). This means that the total porosity of the packed bed is contributed by the interparticle macropores represented by the bed porosity \( \epsilon_b \), and the intraparticle micropores represented by \( (1-\epsilon_b) \epsilon_p \). Each particle is assumed to consist of nanoporous domains (microparticles) interconnected by macropore space. We assume that the macropore space represented by \( \epsilon_b \) is available for the fluid flow of gaseous hydrogen \([19]\).
temperature of the tank wall is set to 302 K. The heat transfer coefficient between steel wall and room temperature water is 36 W/(m² K). The mass flux profile and the hydrogen temperature at entrance are given in Table 4. The basic parameters used in Simulink models are given in Table 5. The specific enthalpies of hydrogen inflow and outflow are obtained from the NIST refpropm function connected with Matlab/Simulink.

### Table 2 - Material properties of adsorbents.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Powder</th>
<th>MOF-5</th>
<th>Compacted MOF-5</th>
<th>Activated carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density, ρw, kg/m³</td>
<td>130</td>
<td>300</td>
<td>269</td>
<td></td>
</tr>
<tr>
<td>Specific heat, c_p, J/kg/K</td>
<td>780</td>
<td>760</td>
<td>825</td>
<td></td>
</tr>
<tr>
<td>Conductivity, k, W/m/K</td>
<td>0.088</td>
<td>0.088</td>
<td>0.764</td>
<td></td>
</tr>
<tr>
<td>Bed porosity, ε</td>
<td>0.246</td>
<td>0.4447</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>Particle diameter, dp, mm</td>
<td>0.36</td>
<td>2.0</td>
<td>2.0</td>
<td></td>
</tr>
</tbody>
</table>

### Table 3 - Material properties of hydrogen and tank wall.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Hydrogen</th>
<th>Steel wall</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density, ρw, kg/m³</td>
<td>Ideal gas</td>
<td>7830</td>
</tr>
<tr>
<td>Specific heat, c_p, J/kg/K</td>
<td>14,700</td>
<td>468</td>
</tr>
<tr>
<td>Conductivity, k, W/m/K</td>
<td>0.206</td>
<td>0.13</td>
</tr>
<tr>
<td>Dynamic viscosity, μ, Pas</td>
<td>8.411e−6</td>
<td>–</td>
</tr>
</tbody>
</table>

### Table 4 - Inlet condition of hydrogen.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Mass flow rate (kg/s)</th>
<th>Mass flux (kg/m²/s)</th>
<th>Hydrogen inflow temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–953</td>
<td>2.048e−5</td>
<td>0.40743666</td>
<td>301.7</td>
</tr>
<tr>
<td>953–3822</td>
<td>0</td>
<td>0</td>
<td>302.5</td>
</tr>
<tr>
<td>3822–4694</td>
<td>−2.186e−5</td>
<td>−0.44348089</td>
<td>297.7</td>
</tr>
<tr>
<td>4694–6000</td>
<td>0</td>
<td>0</td>
<td>298.6</td>
</tr>
</tbody>
</table>

### Table 5 - Parameters of Simulink models.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass of AC, m_ac, kg</td>
<td>0.671</td>
</tr>
<tr>
<td>Mass of powder MOF-5, m_p, kg</td>
<td>0.3246</td>
</tr>
<tr>
<td>Mass of compacted MOF-5, m_c, kg</td>
<td>0.7491</td>
</tr>
<tr>
<td>Mass of tank wall, m_w, kg</td>
<td>3.714</td>
</tr>
<tr>
<td>Volume of tank, V, L</td>
<td>2.4946</td>
</tr>
<tr>
<td>Surface area of tank, A_s, m²</td>
<td>0.1277</td>
</tr>
</tbody>
</table>

#### 3.4 Model validations

The simulation models were validated by a series of tests in the hydrogen storage system with activated carbon, which were performed at Hydrogen Research Institute, University of Quebec at Trois-Rivieres [11–13].

The results of model validation based on the Test No.20 are shown in Fig. 2. The mass balance of activated carbon tank simulated by Comsol is shown in Fig. 2a, where \( m_a \) represents the mass of adsorbed hydrogen in the tank, \( m_t \) represents the mass of gaseous hydrogen, \( m_g \) represents the total mass of hydrogen which is the sum of the initial mass of hydrogen in the tank, the inputting mass of hydrogen and the outputting mass of hydrogen. Good consistency between \( m_t \) and \( m_a + m_g \) can be obtained, which indicates that mass balance of hydrogen in the tank is achieved. At the end of charging, \( m_a \), \( m_t \) and \( m_g \) are 0.0195 kg, 0.011 kg and 0.0085 kg respectively, while the adsorption ratio (adsorbed hydrogen over total hydrogen) is 0.5641.

Fig. 2b–d shows the comparison of pressure, temperatures at the eight monitoring points, thermal average temperature of simulation and experiment for activated carbon tank. Fig. 2b shows that there are good agreements between the pressure calculated by Comsol, Simulink and experiment values. The highest pressure value at the end of discharging reaches 9 MPa, after discharging the system gets into dormancy, the pressure value decreases a little and keeps at 8.6 MPa, then reaches 9 MPa, after charging the system gets into dormancy, the pressure value decreases sharply due to the discharge, after discharging the final pressure value is 0.28 MPa. Fig. 2c shows that there are good consistencies between the simulated temperatures at the eight monitoring points and experiment values. The gap between the simulation and experiment at point Cw may be caused by the heat transfer coefficient between the steel wall and the room temperature water. Fig. 2d shows that the thermal average temperatures calculated by distributed parameter model and lumped parameter model are exactly similar. The results illustrate that the hydrogen storage models are well validated by the Test No. 20.

The model used in this article was widely validated by available experimental results obtained at the storage system packed with activated carbon [11–13,16]. This assures that the fluid flow, heat and mass transfer are well modeled in the model. Further, the model is also validated by metal-organic framework of Cu-BTC [17,18]. It confirms that the model used in this article is also suitable for MOFs such as Cu-BTC. The current work is applying this model to predict the system performance of MOF-5 adsorbents by using appropriate adsorption isotherm models of MOF-5 adsorbents. The experimental system with a new designed tank packed with MOF-5 adsorbents has been set up in Hydrogen Research Institute, University of Quebec at Trois-Rivieres. It will be useful for confirming predicted results of this model.

### 4. Results and discussion

#### 4.1 Distributions of temperature and adsorption in MOF-5 tanks

Fig. 3 shows temperature contours and absolute adsorption contours with velocity arrows at 953s and 4694s in powder MOF-5 and compacted MOF-5 tanks. At 953s, the temperature monitored in the center of the tank is much higher than that at the entrance and near the tank wall. This is due to that the thermal conductivity of MOF-5 bed is much lower than the stainless steel while the heat near the tank wall could transfer to the coolant timely. While at 4694s, the temperature near the tank wall is higher than that in the center of the tank because of the heat transfers from the coolant to the tank. At 953s, the
maximum temperature monitored in the powder MOF-5 tank is much higher than that of compacted MOF-5 tank. At 4694s, the minimum temperature in the powder MOF-5 tank is much lower than that of compacted MOF-5 tank. The higher the temperature goes, the lower the adsorption density is. The adsorption distribution contours of the hydrogen storage tank are opposite to the temperature contours.

4.2. Comparison of hydrogen storage performance of MOF-5 tanks

Fig. 4a shows the mass balance of powder MOF-5 (solid symbol and line) and compacted MOF-5 (empty symbol and line) tanks. Good consistency between $m_t$ and $m_a + m_g$ can be obtained, which indicates mass balance of hydrogen in the tank is achieved. At the end of charging, for powder MOF-5 tank, $m_a$, $m_g$ and $m_s$ are 0.0195 kg, 0.0123 kg and 0.0072 kg, respectively, while for compacted MOF-5 tank, $m_a$, $m_g$ and $m_s$ are 0.0195 kg, 0.0127 kg and 0.0068 kg, respectively. The adsorption ratio of the compacted MOF-5 is higher than the powder MOF-5 at room temperature.

Fig. 4b shows the comparision of the pressures in the MOF-5 (powder and compacted respectively) tanks and AC (activated carbon) tank. The maximal pressure, 15.6 MPa, in the powder MOF-5 tank is much higher than 8.1 MPa in the compacted MOF-5 tank after charging process, due to a larger volume of adsorbed hydrogen in the compacted MOF-5 tank than in the powder MOF-5 tank.

Fig. 4c and d shows the simulated temperatures at the eight monitoring points in powder and compacted MOF-5 tanks, respectively. The highest temperature in powder MOF-5 tank is higher than the one in the compacted MOF-5 tank, and the temperature rising rate is also larger in powder MOF-5 tank during the charging process.

Fig. 5 shows the comparison of pressure and thermal average temperature between Simulink and Comsol in powder and compacted MOF-5 tanks, respectively. The results of Simulink agree well with Comsol. The lumped parameter model implemented by Simulink could be used to predict overall performance of hydrogen storage system.

4.3. Analysis of adsorption heat and pressure work

Fig. 6a shows the isosteric heat of adsorption at point C4 in activated carbon, powder MOF-5 and compacted MOF-5 tanks, respectively, which were calculated by Eq. (16). During the charge process, the quantity of adsorbed hydrogen in unit mass of adsorbent increases with time, and the isosteric heat of adsorption drops slowly. During the dormancy, the isosteric heat of adsorption keeps constant because of the invariability of the absolute adsorption. During the discharge, the isosteric heat of adsorption rises slowly. The isosteric heat of adsorption of activated carbon is the highest among the three materials at the same time.

Fig. 6b and c shows the comparison of adsorption heat and pressure work in three adsorbents. The adsorption heat and pressure work are the $Q$ and $W$ in Eq. (3), respectively.
Fig. 3 – Contours of temperature (left part) and absolute adsorption (right part) with velocity arrows in powder (a, b) and compacted (c, d) MOF-5 tanks at 953s (a, c) and 4694s (b, d).
Fig. 4 – Mass balance analysis (a), pressure comparison (b), and temperatures in powder (c) and compacted (d) MOF-5 tanks simulated by Comsol.

Fig. 5 – Comparison between Simulink and Comsol for pressures (a, c) and thermal average temperatures (b, d) in powder (a, b) and compacted (c, d) MOF-5.
Fig. 6 – Comparison of isosteric heats of adsorption (a), adsorption heats (b) and pressure works (c) for three adsorbents.

Fig. 7 – Mass balance analysis (a), comparison of pressures (b) and thermal average temperatures (c) in cryo-adsorption system.
4.4. Prediction of cryo-adsorption of MOF-5 tanks

The prediction of adsorption hydrogen storage on MOF-5 is made under cryogenic condition. The coolant in Dewar flask is liquid nitrogen at 79 K, the hydrogen charged into the tank is cooled by liquid nitrogen. The charge flow rate from 0s to 385s is 1.3896e4 kg/s, and the discharge flow rate from 9390s to 11,163s is 1.6666e-5 kg/s, the total computing time is 12,000 s.

Fig. 7a shows the mass balance of the powder MOF-5 and compacted MOF-5 tanks cooled by liquid nitrogen. The initial hydrogen masses in the two tanks are 1.91 g and 5.35 g, respectively. At the beginning of charge, for powder MOF-5 tank, $m_{\text{a}}$, $m_{\text{g}}$ and $m_{\text{p}}$ are 0.0555 kg, 0.0399 kg and 0.0156 kg, respectively, which the adsorption ratio is 0.7189, while for compacted MOF-5 tank, $m_{\text{a}}$, $m_{\text{g}}$ and $m_{\text{p}}$ are 0.059 kg, 0.0512 kg and 0.0078 kg, respectively, which the adsorption ratio is 0.8678.

For compacted MOF-5 adsorbent, adsorbed hydrogen amount increases from 0.0127 kg to 0.0512 kg when its storage condition changed from room temperature to cryogenic temperature. That is four-fold increase of adsorption amount and the storage pressure is lower. So that the cryo-adsorption of hydrogen on compacted MOF-5 is very advantageous.

Fig. 7b shows the comparison of the pressures in the two MOF-5 (powder and compacted MOF-5) tanks with activated carbon tank. After charging, the highest pressures of the two MOF-5 tanks are 16.0 MPa and 6.1 MPa respectively. Fig. 7c shows the comparison of thermal average pressures in powder and compacted MOF-5 tank, respectively.

The boundary and initial conditions used in the simulations took the Test No. 20 as reference, in which the operating conditions adopted almost the same charge flow rate and discharge flow rate. The charge flow rate can be larger during fast filling of a tank. In this section, the charge flow rate 1.3896e4 kg/s is much larger than the discharge flow rate 1.6666e-5 kg/s. However, the adsorption rate and desorption rate will be controlled by the temperature and pressure in the tank and kinetic feature of adsorbent.

5. Conclusions

We studied hydrogen storage processes of MOF-5 hydrogen storage systems with adsorbents of both the MOF-5 powder (0.13 g/cm³) and its compacted tablet (0.30 g/cm³). The charge–discharge cycle of these two MOF-5 adsorbents were simulated and compared with activated carbon.

(1) The heat and mass transfer feature of the model was validated by the experiments of activated carbon. The simulated pressures and temperatures are in a good agreement with the experimental values for activated carbon.

(2) The pressure and temperature profiles predicted by Comsol agree very well with experimental results. The Simulink predictions give agreeable pressures and temperatures with Comsol simulation and experimental pressures for both powder and compacted MOF-5 adsorbents.

(3) The maximum pressure in the powder MOF-5 tank is much higher than that of activated carbon due to the lower adsorbent density and resulting lower hydrogen adsorption. The maximum pressure in the compacted MOF-5 tank is a little bit lower than that of activated carbon due to the higher adsorbent density and resulting higher hydrogen adsorption.

(4) The temperature swings of both MOF-5 materials are higher than that of activated carbon. The higher temperature swings are caused mainly by pressure work in powder MOF-5 and by adsorption heat in compacted MOF-5.

(5) The compacted MOF-5 cryo-adsorption hydrogen storage system is advantageous since it can store more hydrogen at lower pressure and with less temperature rise.

(6) Validation tests of MOF-5 hydrogen system are expected to be performed in order to optimize the lumped parameter and multi-dimensional models.

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References


